U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

AD-A024 258

ELECTRONIC ANGULAR MOMENTUM TRANSFER IN THE I(DOUBLETP($\frac{1}{2}$) + NF (A SINGLET DELTA) SYSTEM

AEROSPACE CORPORATION

PREPARED FOR
SPACE AND MISSILE SYSTEMS ORGANIZATION

17 MARCH 1976

REPORT SAMSO-TR-76-58

Electronic Angular Momentum Transfer in the $I(^2P_{1/2}) + NF(a^1\Delta)$ System

JOHN M. HERBELIN and M. A. KWOK
Aerophysics Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, Calif. 90245

17 March 1976

Interim Report

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED

Prepared for
SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE | READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: SAMSO-TR-76-58
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER:
4. TITLE (and Subtitle): ELECTRONIC ANGULAR MOMENTUM TRANSFER IN THE $I(^2P_{1/2})$ + $NF(a^1\Delta)$ SYSTEM
5. TYPE OF REPORT & PERIOD COVERED: Interim
6. PERFORMING ORG. REPORT NUMBER: TR-0076(6240-40)-4
7. AUTHOR(s): John M. Herbelin and Munson A. Kwok
8. CONTRACT OR GRANT NUMBER(s): F04701-75-C-0076
9. PERFORMING ORGANIZATION NAME AND ADDRESS: The Aerospace Corporation, El Segundo, Calif. 90245
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
11. CONTROLLING OFFICE NAME AND ADDRESS: Space and Missile Systems Organization, Air Force Systems Command, Los Angeles, Calif. 90009
12. REPORT DATE: 17 March 1976
13. NUMBER OF PAGES: 7
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):
15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:
16. DISTRIBUTION STATEMENT (of this Report): Approved for public release; distribution unlimited.
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):
18. SUPPLEMENTARY NOTES:
19. KEY WORDS (Continue on reverse side if necessary and identify by block number):
Nitrogen Fluoride
Energy Transfer, Electronic States of Nitrogen Fluoride
Electronic Energy Transfer
Iodine Atoms
Atom-Molecule Energy Transfers
20. ABSTRACT (Continue on reverse side if necessary and identify by block number):

A rate coefficient at 298 K of $>2.6 \times 10^{14}$ cm^3-mol^{-1}-sec^{-1} has been deduced for the electronic energy transfer:

$$I(^2P_{1/2}) + NF\,(a^1\Delta) \rightarrow I(^2P_{3/2}) + NF(b^1\Sigma^+)$$

DD FORM 1473 (FACSIMILE)

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract F04701-75-C-0076 with the Space and Missile Systems Organization, Deputy for Advanced Space Programs, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. R. Warren, Jr., Director, Aerophysics Laboratory. Lt. Ronald C. Lawson, SAMSO/DYN, was the project officer.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER

Ronald C. Lawson

Ronald C. Lawson
1st Lt., United States Air Force
Research Applications Directorate
Deputy for Advanced Space Programs

PREFACE

The authors acknowledge the assistance of R. H. Ueunten in the experiment.

CONTENTS

Preceding page blank

ELECTRONIC ANGULAR MOMENTUM TRANSFER IN THE $I(^2P_{1/2}) + NF(a^1\Delta)$ SYSTEM

Evidence has been observed for a nearly gaskinetic rate coefficient for the E-E transfer:

$$I(^2P_{1/2}) + NF(a^1\Delta) \rightarrow I(^2P_{3/2}) + NF(b^1\Sigma^+) + 110\ cm^{-1} \tag{1}$$

by using the large-diameter, medium-pressure flow tube facility.[1] Such a large rate coefficient had been anticipated by previous studies[*,**,2] that describe the role of electronic spin conservation in the reactive $F + H_2$/$H + NF_2$ systems in producing NF electronically excited species.[**,2] The experiment involves determination of the axial variations of $NF(a^1\Delta)$ and $NF(b^1\Sigma^+)$ number densities in a sequence of carefully selected reagent flow conditions. This is followed by observation of the $(a^1\Delta\text{-}X^3\Sigma^-)$ and $(b^1\Sigma^+ - X^3\Sigma^-)$ spontaneous emissions in the axially translating reaction zone. The enhancement of $NF(b^1\Sigma^+)$ by the presence of $I(^2P_{1/2})$ can then be observed, and an estimate can be made of the rate coefficient by using a chemical kinetic model that fits the experimental number densities.

From the passage of $Ar + NF_3$ through an rf discharge, F and 1% NF_2 are produced, which can be reacted with D_2 and HI injected rapidly into the principal flow from an axially movable tee injector located on the tube centerline. The reaction $F + D_2$ yields D atoms in excess, which, in turn, react with NF_2 to predominantely produce[2] $NF(a^1\Delta)$. The excess D also rapidly

---

[*] J. M. Herbelin, "The Role of Electron Spin in the NF System," to be published.

[**] M. A. Kwok, J. M. Herbelin, and N. Cohen "Collisional Quenching and Radiative Decay Studies of $NF(a^1\Delta)$ and $NF(b^1\Sigma^+)$," to be published.

[1] Munson A. Kwok and Roger L. Wilkins, J. Chem. Phys. 63, 2453 (1975).

[2] J. M. Herbelin and N. Cohen, Chem. Phys. Lett. 20, 605 (1973).

Preceding page blank

reacts with HI to produce mainly $I(^2P_{3/2})$ atoms.[3,4] In order to generate sufficient $I(^2P_{1/2})$, it is necessary to pass O_2 through a 2.45 GHz microwave cavity some distance upstream of the reaction zone to yield $O_2(a^1\Delta)$. The O atoms are suppressed by the heated mercuric oxide coating in the quartz sidearm. The transfer $O_2(a^1\Delta) + I(^2P_{3/2})$ is known to be extremely rapid[5] for the efficient production of $I(^2P_{1/2})$.

Flow conditions are chosen such that $O_2(a^1\Delta)$ is excess to I for ease of analysis, but not in sufficient excess to obliterate evidence of the $I(^2P_{1/2})$ + $NF(a^1\Delta)$ transfer by the alternative process[2] $O_2(a^1\Delta) + NF(a^1\Delta)$. Typical reagent flowrates for Case 4 in Fig. 1 would be in μmol-sec^{-1}: F, 15; NF_2, 0.15; O_2, 50; D_2, 150; HI, 0.08. Experience[6,7] indicates that the amount of $O_2(a^1\Delta)$ generated in the usual 2.45 GHz 70 W microwave is 5% of O_2. The tube operates at 1 Torr, 298 K and 6800 cm sec^{-1}. Case 1 is a previously used baseline.[2] Cases 2 and 3 verify the necessity of the simultaneous presence, in Case 4, of $O_2(a^1\Delta)$ and I for significant pumping of $NF(b^1\Sigma^+)$. The axial number density plot of $NF(b^1\Sigma^+)$ versus Z shown in Fig. 1 for Case 4 shows this strong pumping. We interpret Case 4 to mean that $I(^2P_{1/2})$ is rapidly produced with the presence of $O_2(a^2\Delta)$ and then rapid transfer occurs, as described by Eq. (1). Axial number density plots of $NF(a^1\Delta)$ for Cases 1 through 4 are virtually identical. $NF(a^1\Delta)$ behaves as a reservoir because, in all cases, the $NF(b^1\Sigma^+)$ is at most only 1% of observed $NF(a^1\Delta)$ concentrations.

A quantitative estimate of the transfer rate coefficient for Eq. (1) can be made. The growth of $NF(b^1\Sigma^+)$ for Case 4 in Fig. 1 is found to be quadratic in Z (or time). This implies that either $NF(a^1\Delta)$ or $I(^2P_{1/2})$ is in a

---

[3] W. E. Jones, S. D. MacKnight, and Lo Teng, Chem. Rev. 73, 407 (1973).
[4] P. Cadman and J. C. Polanyi, J. Phys. Chem. 72, 3715 (1968).
[5] R. G. Derwent and B. A. Thrush, Chem. Soc. Faraday Disc. 53, 162 (1972).
[6] R. G. Derwent and B. A. Thrush, Trans. Faraday Soc. 67, 2036 (1971).
[7] L. W. Bader and E. A. Ogryzlo, Disc. Faraday Soc. 37, 46 (1964).

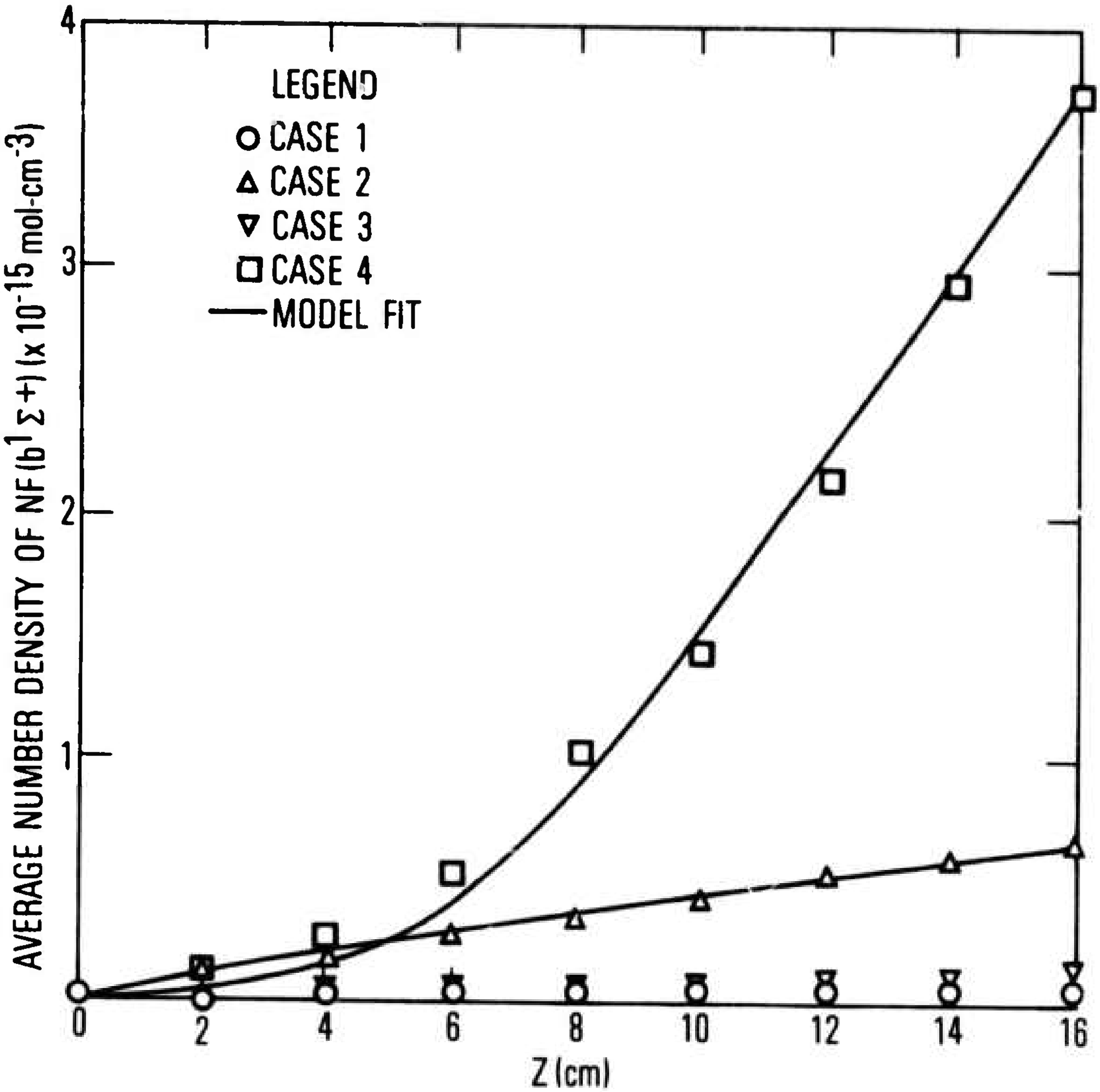

Figure 1. Axial Variations of the Number Densitv of $NF(b^1\Sigma^+)$, Averaged Along the Tube Diameter. Case 1: F, NF_2, D_2, O_2. Case 2: F, NF_2, D_2, O_2, $O_2(a^1\Delta)$. Case 3: F, NF_2, D_2, O_2, HI. Case 4: F, NF_2, D_2, O_2, $O_2(a^1\Delta)$, HI. The solid lines represent model fits.

linear region of growth. A simple five-kinetic equation analysis for the one unknown rate shows that the lower bound for k_1, in Eq. (1), is 2.6×10^{14} $cm^3 mol^{-1} sec^{-1}$. The estimate is a bound because the absolute $O_2(a^1\Delta)$ density has not been measured but has been assumed to be $\leq 5\%$ of O_2, and k_1 is inversely proportional to $O_2(a^1\Delta)$. A more detailed description of this study will be given elsewhere.

LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military concepts and systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space and missile systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch and reentry aerodynamics, heat transfer, reentry physics, chemical kinetics, structural mechanics, flight dynamics, atmospheric pollution, and high-power gas lasers.

Chemistry and Physics Laboratory: Atmospheric reactions and atmospheric optics, chemical reactions in polluted atmospheres, chemical reactions of excited species in rocket plumes, chemical thermodynamics, plasma and laser-induced reactions, laser chemistry, propulsion chemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, photosensitive materials and sensors, high precision laser ranging, and the application of physics and chemistry to problems of law enforcement and biomedicine.

Electronics Research Laboratory: Electromagnetic theory, devices, and propagation phenomena, including plasma electromagnetics; quantum electronics, lasers, and electro-optics; communication sciences, applied electronics, semiconducting, superconducting, and crystal device physics, optical and acoustical imaging; atmospheric pollution, millimeter wave and far-infrared technology.

Materials Sciences Laboratory: Development of new materials; metal matrix composites and new forms of carbon; test and evaluation of graphite and ceramics in reentry; spacecraft materials and electronic components in nuclear weapons environment; application of fracture mechanics to stress corrosion and fatigue-induced fractures in structural metals.

Space Sciences Laboratory: Atmospheric and ionospheric physics, radiation from the atmosphere, density and composition of the atmosphere, aurorae and airglow; magnetospheric physics, cosmic rays, generation and propagation of plasma waves in the magnetosphere; solar physics, studies of solar magnetic fields: space astronomy, x-ray astronomy; the effects of nuclear explosions, magnetic storms, and solar activity on the earth's atmosphere, ionosphere, and magnetosphere; the effects of optical, electromagnetic, and particulate radiations in space on space systems.

THE AEROSPACE CORPORATION
El Segundo, California